Silicas precipitated by a specific method for rubber applications

The present invention relates to precipitated silicas which have extremely low microporosity and high rubber activity, to a process for their preparation, and to their use as filler for rubber mixtures.

The use of precipitated silicas in elastomer mixtures, such as tire tread mixtures, has been known for a long time (EP 0 501 227). There are stringent requirements relating to the use of silicas as a reinforcing filler in rubber mixtures, for example those used to produce pneumatic tires and technical rubber products. They have to have low density and have good capability for incorporation and dispersion in the rubber, and undergo chemical bonding to the rubber in association with a coupling reagent, preferably a bifunctional organosilicon compound, this reaction leading to the desired high level of reinforcement of the rubber mixture. The property of reinforcement can in particular be associated with high static stress values and a low abrasion value. The particle size, surface morphology, surface activity, and also the binding power of the coupling reagent, are of particularly decisive importance in relation to the reinforcing property of the silicas.

Precipitated silicas with primary particle diameters of from 10 to 50 nm are usually used in rubber applications. One way of determining the primary particle diameter is by means of transmission electron spectroscopy (TEM) image evaluation (R. H. Lange, J. Bloedorn: "Das Elektronenmikroskop, TEM + REM" [The electron microscope, TEM + SEM] Thieme Verlag, Stuttgart, New York (1981)). The surface areas are measured via the adsorption of the small nitrogen molecule N_2, and are termed BET surface area below

(S. Brunauer, P. H. Emmett, E. Teller, "Adsorption of Gases in Multimolecular Layers", J. Am. Chem. Soc. 60, 309 (1938)), and are typically in the range from 50 to 200 m^2/g, preferably from 110 to 180 m^2/g. The surface area accessible to the rubber, hereinafter termed the CTAB surface area, is determined by means of the adsorption of the larger N-cetyl-N,N,N-trimethyl-ammonium bromide molecule (See Janzen, Kraus, Rubber Chem. Technol. 44, 1287 (1971)). Detailed information describing exactly how the measurements are made is given in the following text. The difference between the BET surface area and the CTAB surface area can therefore be termed the microporosity, and represents the silica surface area inaccessible to the rubber and therefore ineffective for reinforcement. In commercially available active silicas the BET/CTAB ratio is usually > 1.05, indicating a correspondingly high degree of microporosity.

In addition, the skilled worker is aware that low-molecular-weight compounds, e.g. the bifunctional organosilicon compounds and vulcanization accelerators, can undergo physi- and chemisorption within the pores of the microporous silica, and thus lose their ability to carry out their function as coupling agent for the rubber or vulcanization accelerator for crosslinking of the rubber.

The skilled worker is also aware that the coupling reagent, usually a bifunctional organosilicon compound known from S. Wolff, "Chemical Aspects of Rubber Reinforcement by Fillers", Rubber Chem. Technol. 69, 325 (1996), is intended to modify the rubber-active surface quantitatively and with maximum uniformity. The modification may take place via precoating of the silica in bulk or in solution/suspension (ex situ) (U. Görl, R. Panenka, "Silanisierte Kieselsäuren - Eine neue Produktklasse für zeitgemässe Mischungsent-

wicklung" (Silanized silicas – a new product class for advanced compound development), Kautsch. Gummi Kunstst. **46**, 538 (1993)), or else during the mixing process (in situ) (H.-D. Luginsland, "Processing of Silica/Silane-Filled Tread Compounds", paper No. 34 presented at the ACS Meeting, April 4-6, 2000, Dallas, Texas/USA), in situ modification being the preferred and usually used process. To ensure rapid and quantitative silanization of the rubber-active surface, it is therefore necessary to enrich the surface in a controlled manner with reactive silanol groups to which the organosilicon compound can bond. The interaggregate structure of silicas is usually determined by means of the DBP test (J. Behr, G. Schramm, "Über die Bestimmung der Ölzahl von Kautschukfüllstoffen mit dem Brabender-Plastographen" (Determination of the oil value of rubber fillers using the Brabender Plastograph], Gummi Asbest Kunstst. 19, 912 (1966)). A high DBP value is needed to ensure ideal dispersion of the filler in the rubber. A moisture level > 4% is needed to ensure rapid and complete silanization of the silica surface with an organosilicon compound (U. Görl, A. Hunsche, A. Müller, H. G. Koban, "Investigations into the Silica/Silane Reaction System", Rubber Chem. Technol. 70, 608 (1997)).

JP 2002179844 discloses rubber mixtures with silicas in which the difference between BET surface area and CTAB surface area of the silicas is smaller than 15 m^2/g. No mention is made of the high Sears value V_2, this being a measure of the number of silanol groups needed for high activity with respect to the bifunctional organosilicon compound, or of the high DBP value needed for very good dispersion in the rubber. However, these two values, alongside the low microporosity, are decisive for a high degree of reinforcement of the rubber mixture and therefore good road abrasion properties.

The skilled is worker is aware of various processes for
preparing silicas. For example, EP 0 937 755 describes
precipitations at constant pH. DE 101 24 298 discloses
silicas precipitated at constant cation excess. DE 101
5   12 441 A1, EP 0 755 899 A2, and US 4 001 379 describe
precipitations at constant alkali value (AV value).

Silicas for rubber applications are generally prepared
by a process in which the precipitation takes place at
10   temperatures of from 60 to 95°C and at a non-constant
pH of from 7 to 10, see EP 0 901 986 A1, for example.

It is an object of the present invention to provide
novel, readily dispersible precipitated silicas which
15   can be incorporated in elastomer mixtures and which
improve their properties. A further intention is to
provide a process for preparing these silicas.

The present invention therefore provides readily
20   dispersible precipitated silicas characterized by:

CTAB surface area $\qquad$ 100-200 m^2/g, the preferred
ranges being 100-160 m^2/g,
100-130 m^2/g, and 110-125
m^2/g,

25   BET/CTAB ratio $\qquad$ 0.8-1.05, preferred ranges
0.90-1.03, 0.93-1.03, and
particularly 0.96-1.03,

DBP value $\qquad$ 210-280 g/(100 g), prefer-
red range 250-280 g/
30   (100 g),

Sears value V_2 $\qquad$ 10-30 ml/(5 g), the
preferred ranges being
20-30 ml/(5 g)and 21 to 28
(ml/5 g),

35   Moisture level $\qquad$ 4-8%.

The precipitated silicas of the invention may moreover
preferably have one or more of the following physico-

chemical parameters:

BET surface area	80-210 m^2/g, the precipitated silicas in a first embodiment having a BET of 80-110 m^2/g and those in a second embodiment having a BET of 110-150 m^2/g, preferably 110-129 m^2/g,
Ratio of Sears value V_2 to BET surface area	0.140-0.370 ml/(5 m^2), the preferred ranges being 0.150-0.320 ml/(5 m^2), 0.170-0.320 ml/(5 m^2), 0.180-0.300 ml/(5 m^2), particularly preferably 0.190-0.280 ml/(5 m^2) and 0.190-0.240 ml/(5 m^2),
Primary particle diameter	10-50 nm.

In one preferred embodiment, the precipitated silicas of the invention have a Sears value V_2 of 22-25 ml/(5 g), the Sears value V_2 in another embodiment being 25-28 ml/(5 g).

The precipitated silicas of the invention have not only a high absolute number of silanol groups (Sears value V_2), but also, when comparison is made with prior-art precipitated silicas, a markedly increased ratio of the Sears value V_2 to the BET surface area. This means that the precipitated silicas of the invention in particular have a very high number of silanol groups based on the total surface area.

The precipitated silicas of the invention have not only an increased number of silanol groups but also low microporosity, i.e. a very low ratio of BET to CTAB.

The combination of the features mentioned, in particular the high ratio of Sears value V_2 to BET, gives the precipitated silicas of the invention excellent suitability as reinforcing fillers for elastomers. These precipitated silicas of the invention have increased rubber activity, and exhibit very good dispersion behavior and a low vulcanization time.

The present invention further provides a process which can be used to prepare the precipitated silicas of the invention with

CTAB surface area	100-200 m^2/g, the preferred ranges being 100-160 m^2/g, 100-130 m^2/g, and 110-125 m^2/g,
BET/CTAB ratio	0.8-1.05, preferred ranges 0.90-1.03, 0.93-1.03, and particularly 0.96-1.03,
DBP value	210-280 g/(100 g), preferred range 250-280 g/(100 g),
Sears value V_2	10-30 ml/(5 g), the preferred ranges being 20-30 ml/(5 g) and 21 to 28 (ml/5 g),
Moisture level	4-8%,

and, where appropriate, with one or more of the following physico-chemical parameters

BET surface area	80-210 m^2/g, the precipitated silicas in a first embodiment having a BET of 80-110 m^2/g and those in a second embodiment having a BET of 110-150 m^2/g, preferably 110-129 m^2/g,
Ratio of Sears value V_2	

to BET surface area $0.140-0.370$ ml/(5 m^2), the preferred ranges being $0.150-0.320$ ml/(5 m^2), $0.170-0.320$ ml/(5 m^2), $0.180-0.300$ ml/(5 m^2), particularly preferably $0.190-0.280$ ml/(5 m^2) and $0.190-0.240$ ml/(5 m^2),

primary particle diameter   10-50 nm,

which comprises first

a)   taking an aqueous solution of an alkali metal silicate or alkaline earth metal silicate and/or of an organic and/or inorganic base with pH from 7 to 14 as initial charge,

b)   metering water glass and an acidifier simultaneously into this initial charge at from 55 to 95°C, with stirring, for from 10 to 120 minutes, preferably from 10 to 60 minutes,

g)   continuing to stir the resultant suspension at from 80 to 98°C, for from 1 to 120 minutes, preferably from 10 to 60 minutes,

h)   using an acidifier to acidify to pH of from 2.5 to 5, and

i)   filtering, washing, drying and, where appropriate, pelletizing.

The initial charge may amount to about 20, 30, 40, 50, 60, 70, 80, or 90% of the final volume for the precipitation. The basic compounds for the initial charge are in particular selected from the group of the alkali metal hydroxides, alkaline earth metal hydroxides, alkali metal carbonates, alkali metal hydrogencarbonates, and alkali metal silicates. Preference is given to the use of water glass and/or sodium hydroxide solution. The pH of the initial charge is from 7 to 14, preferably from 10 to 11.

The manner of adding the water glass and the acidifier
during step b) may be such that the pH of the reaction
solution is held constant or remains variable. However,
it is also possible for the precipitation to take place
5 at a constant alkali value. If the precipitation takes
place at a constant pH, this is preferably in the range
from 7 to 11. Precipitations at a constant alkali value
preferably take place at an alkali value of from 15 to
40.

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After step b) the process of the invention may comprise
one or two hold points, viz.:

c)   stopping the feed for from 30 to 90 minutes while
      maintaining the temperature, and

15 d)   then, where appropriate, simultaneously feeding
      water glass and an acidifier at the same
      temperature, with stirring, for from 20 to 120
      minutes, preferably from 20 to 80 minutes.

20 Following step b) or d) of the process of the
invention, addition of water glass is stopped and, if
the desired pH has not yet been achieved, in step

e)   the acidifier feed is continued at an identical or
25   different rate until a pH of 5 to 11, preferably
      from 7 to 10, has been achieved.

In order to vary the concentration of the water glass
available for the reaction, where appropriate,

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f)   the pH may be adjusted to from 3 to 11 by adding
      further acidifier, and/or raised again to values
      of from 8 to 14, preferably 9-10, and particularly
      7-11, via feed of one or more basic compounds from
35   the group of the alkali metal hydroxides, alkaline
      earth metal hydroxides, alkali metal carbonates,
      alkali metal hydrogencarbonates, and alkali metal
      silicates. Use of water glass and/or sodium

hydroxide solution is preferred.

The feed of the acidifier in step e) or of the basic
compound in step f) may take place at from 40 to 98°C.
5   The feed preferably takes place at from 55 to 95°C and
particularly preferably at the temperature also
selected for step b) or d).

Another hold point may optionally be incorporated
10 between steps d) and e).

Another addition of organic or inorganic salts may
moreover optionally be incorporated during one or more
of steps a) to h). This addition may be carried out in
15 solution or in solid form, in each case continuously
over the period of addition of the water glass and of
the acidifier, or may be batch addition. It is also
possible for the salts to be dissolved in one or both
of the components and then to be added simultaneously
20 with these.

The inorganic salts preferably used are alkali metal
salts or alkaline earth metal salts. In particular, use
may be made of any of the combinations of the following
25 ions:
Li^+, Na^+, K^+, Rb^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, H^+, F^-, Cl^-,
Br^-, I^-, SO_3^{2-}, SO_4^{2-}, HSO_4^-, PO_3^{3-}, PO_4^{3-}, NO_3^-, NO_2^-, CO_3^{2-},
HCO_3^-, OH^-, TiO_3^{2-}, ZrO_3^{2-}, ZrO_4^{4-}, AlO_2^-, $Al_2O_4^{2-}$, BO_4^{3-}.
Suitable organic salts are the salts of formic, acetic,
30 or propionic acid. Cations which may be mentioned are
the abovementioned alkali metal ions or alkaline earth
metal ions. The concentration of these salts in the
solution added may be from 0.01 to 5 mol/l. The
inorganic salt preferably used is Na_2SO_4.

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The manner of introducing the acidifier in steps b) and
d) may be identical or different, i.e. its
concentration and/or feed rate may be identical or

different.

Similarly, a manner of introducing the water glass to the reaction in steps b) and d) may be identical or different.

In one particular embodiment, the manner of introducing the components acidifier and water glass in steps b) and d) is such that the feed rate in step d) is from 125 to 140% of the feed rate in step b), each of the components being used in equimolar concentration in the two steps. It is preferable for the components to be added with identical concentration and feed rate.

Besides water glass (sodium silicate solution), use may also be made of other silicates, such as potassium silicate or calcium silicate. Acidifiers which may be used, besides sulfuric acid, are HCl, HNO_3, H_3PO_4, or CO_2.

The filtration and long-term or short-term drying of the silicas of the invention are matters familiar to the skilled worker and can be found in the documents mentioned, for example.

The silica precipitated is preferably dried in a pneumatic drier, spray drier, disk drier, belt drier, rotating-tube drier, flash drier, spin flash drier, or spray tower. These drying methods include operation using an atomizer, using a single- or twin-fluid nozzle, or using an integrated fluidized bed. Where appropriate, after the drying process grinding may take place, and/or a roller compactor may be used for palletizing. After the drying step, the grinding, or the pelletization, the precipitated silica of the invention preferably has a particle shape with an average diameter above 15 µm, in particular above 80 µm, particularly preferably above 200 µm (determined

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ISO 2591-1, December 1988). The precipitated silicas of
the invention particularly preferably take the form of
a powder with an average diameter above 15 μm, or take
the form of substantively round particles with an
5 average diameter above 80 μm (microbeads), or take the
form of pellets with an average diameter $\geq$ 1 mm.

The present invention also provides the use of the
precipitated silicas of the invention, with a

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CTAB surface area   100-200 m^2/g, the preferred
                                ranges being 100-160 m^2/g,
                                100-130   m^2/g,   and
                                110-125 m^2/g,

15 BET/CTAB ratio   0.8-1.05, preferred ranges
                                0.90-1.03, 0.93-1.03, and
                                particularly   preferably
                                0.96-1.03,

DBP value   210-280   g/(100   g),
20   preferred   range
                                250-280 g/(100 g),

Sears value V$_2$ 10-30   ml/(5   g),   the
                                preferred   ranges   being
                                20-30 ml/(5 g)and 21 to 28
25   (ml/5 g),
Moisture level   4-8%

and also, where appropriate, with one or more of the
following physico-chemical parameters

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BET surface area   80-210   m^2/g,   the
                                precipitated silicas in a
                                first embodiment having a
                                BET of 80-110 m^2/g and
35   those in a second
                                embodiment having a BET of
                                110-150 m^2/g, preferably
                                110-129 m^2/g,

Ratio of Sears value V_2
to BET surface area   0.140-0.370 ml/(5 m^2), the
                                       preferred   ranges   being
                                       0.150-0.320 ml/(5 m^2),
5   0.170-0.320 ml/(5 m^2),
                                       0.180-0.300   ml/(5   m^2),
                                       particularly   preferably
                                       0.190-0.280 ml/(5 m^2) and
                                       0.190-0.240 ml/(5 m^2),
10   primary particle diameter   10-50 nm

for preparing elastomer mixtures, vulcanizable rubber
mixtures, and/or other vulcanisates.

15   The invention therefore also provides elastomer
mixtures, vulcanizable rubber mixtures, and/or other
vulcanizates which comprise the silica of the
invention, examples being moldings, such as pneumatic
tires, tire treads, cable sheathing, hoses, drive
20   belts, conveyor belts, roller coverings, tires, shoe
soles, ring seals, and damping elements.

The silicas of the invention may also be used in any of
the application sectors which usually use silicas, e.g.
25   in battery separators, as antiblocking agent, as
matting agent in inks and paints, as carrier for
agricultural products and for feeds, in coatings, in
printing inks, in fire-extinguisher powders, in
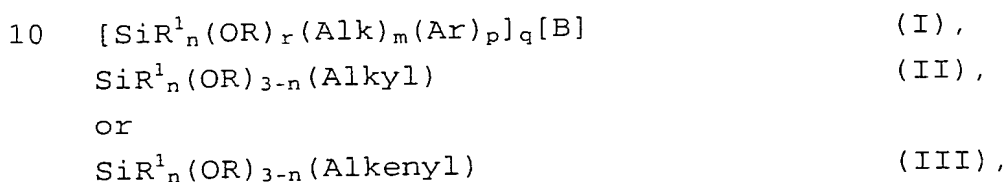plastics, in the non-impact printing sector, in paper
30   pulp, or in the personal care sector, or in specialty
applications. Use in the non-impact printing sector,
for example in inkjet printing, is use of the silicas
of the invention in
     • printing inks for thickening or for preventing
35   splashing and offset,
     • paper, as filler or coating pigment, blueprint paper,
       heat-sensitive paper, thermal sublimation for
       preventing strike-through of printing inks, for

improvement in contrast and image background uniformity, and for improvement in dot definition and color brilliance.

Use in the personal care sector is use of the silicas of the invention as filler or thickener, e.g. in the pharmaceutical sector or the body-care sector.

The silica of the invention may optionally be modified with silanes or organosilanes of the formulae I to III

$$[SiR^1_n(OR)_r(Alk)_m(Ar)_p]_q[B] \quad\quad (I),$$
$$SiR^1_n(OR)_{3-n}(Alkyl) \quad\quad (II),$$
or
$$SiR^1_n(OR)_{3-n}(Alkenyl) \quad\quad (III),$$

where

B   is -SCN, -SH, -Cl, -NH$_2$, -OC(O)CHCH$_2$, -OC(O)C(CH$_3$)CH$_2$ (if q = 1), or -S$_w$- (if q = 2), B being chemically bonded to Alk,

R and R^1 are an aliphatic, olefinic, aromatic, or arylaromatic radical having 2-30 carbon atoms, optionally with substitution by the following groups: the hydroxyl, amino, alcoholate, cyanide, thiocyanide, halo, sulfonic acid, sulfonic ester, thiol, benzoic acid, benzoic ester, carboxylic acid, carboxylic ester, acrylate, methacrylate, or organosilane radical, where the meaning or substitution of R and R^1 may be identical or different,

n   is 0, 1, or 2,

Alk   is a bivalent unbranched or branched hydro-carbon radical having from 1 to 6 carbon atoms,

m   is 0 or 1,

Ar   is an aryl radical having from 6 to 12 carbon atoms, preferably 6 carbon atoms, which may have substitution by the following groups: the hydroxyl, amino, alcoholate, cyanide, thio-cyanide, halo, sulfonic acid, sulfonic ester,

thiol, benzoic acid, benzoic ester, carboxylic acid, carboxylic ester, or organosilane radical,

p   is 0 or 1; with the proviso that p and n are not simultaneously 0,

q   is 1 or 2,

w   is a number from 2 to 8,

r   is 1, 2, or 3, with the proviso that $r + n + m + p = 4$,

Alkyl   is a monovalent unbranched or branched saturated hydrocarbon radical having from 1 to 20 carbon atoms, preferably from 2 to 8 carbon atoms,

Alkenyl   is a monovalent unbranched or branched unsaturated hydrocarbon radical having from 2 to 20 carbon atoms, preferably from 2 to 8 carbon atoms.

The silica of the invention may also be modified with organosilicon compounds of the composition $SiR^2_{4-n}X_n$ (where $n = 1, 2, 3, 4$), $[SiR^2_xX_yO]_z$ (where $0 \leq x \leq 2$; $0 \leq y \leq 2$; $3 \leq z \leq 10$, where $x + y = 2$), $[SiR^2_xX_yN]_z$ (where $0 \leq x \leq 2$; $0 \leq y \leq 2$; $3 \leq z \leq 10$, where $x + y = 2$), $SiR^2_nX_mOSiR^2_oX_p$ (where $0 \leq n \leq 3$; $0 \leq m \leq 3$; $0 \leq o \leq 3$; $0 \leq p \leq 3$, where $n + m = 3$, $o + p = 3$), $SiR^2_nX_mNSiR^2_oX_p$ (where $0 \leq n \leq 3$; $0 \leq m \leq 3$; $0 \leq o \leq 3$; $0 \leq p \leq 3$, where $n + m = 3$, $o + p = 3$), $SiR^2_nX_m[SiR^2_xX_yO]_zSiR^2_oX_p$ (where $0 \leq n \leq 3$; $0 \leq m \leq 3$; $0 \leq x \leq 2$; $0 \leq y \leq 2$; $0 \leq o \leq 3$; $0 \leq p \leq 3$; $1 \leq z \leq 10000$, where $n + m = 3$, $x + y = 2$, $o + p = 3$). These compounds may be linear, cyclic, or branched, silane, silazane, or siloxane compounds. R^2 may be substituted and/or unsubstituted alkyl and/or aryl radicals, in each case having 1-20 carbon atoms, which may have substitution by functional groups, for example by the hydroxyl group, by the amino group, by polyethers, such as ethylene oxide and/or propylene oxide, or by halide groups, such as fluoride. R^2 may also include groups such as alkoxy, alkenyl, alkynyl,

and aryl groups, and sulfur-containing groups. X may be reactive groups, such as the silanol, amino, thiol, halogen, alkoxy, and alkenyl groups, and the hydrogen radical.

Preference is given to linear polysiloxanes of composition $SiR^2_nX_m[SiR^2_xX_yO]_zSiR^2_oX_p$ (where $0 \leq n \leq 3$; $0 \leq m \leq 3$; $0 \leq x \leq 2$; $0 \leq y \leq 2$; $0 \leq o \leq 3$; $0 \leq p \leq 3$; $1 \leq z \leq 10000$, where $n + m = 3$; $x + y = 2$; $o + p = 3$), R^2 preferably being methyl.

Particular preference is given to polysiloxanes of composition $SiR^2_nX_m[SiR^2_xX_yO]_zSiR^2_oX_p$ (where $0 \leq n \leq 3$; $0 \leq m \leq 1$; $0 \leq x \leq 2$; $0 \leq y \leq 2$; $0 \leq o \leq 3$; $0 \leq p \leq 1$; $1 \leq z \leq 1000$, where $n + m = 3$, $x + y = 2$, $o + p = 3$), R^2 preferably being methyl.

The modification of the optionally pelletized, unpelletized, ground, and/or unground precipitated silica with one or more of the organosilanes mentioned may take place in mixtures of from 0.5 to 50 parts, based on 100 parts of precipitated silica, in particular from 1 to 15 parts, based on 100 parts of precipitated silica, where the reaction between precipitated silica and organosilane may be carried out during preparation of the mixture (in situ) or externally via spray application and subsequent heat-conditioning of the mixture, via mixing of the organosilane and the silica suspension with subsequent drying and heat-conditioning (e.g. as in DE 34 37 473 and DE 196 09 619), or by the process described in DE 196 09 619 or DE-C 40 04 781.

Suitable organosilicon compounds are in principle any of the bifunctional silanes which firstly can bring about coupling to the filler containing silanol groups and secondly can bring about coupling to the polymer. Amounts usually used as the organosilicon compounds are

from 1 to 10% by weight, based on the total amount of precipitated silica.

Examples of these organosilicon compounds are:
bis(3-triethoxysilylpropyl) tetrasulfane, bis(3-triethoxysilylpropyl) disulfane, vinyltrimethoxysilane, vinyltriethoxysilane, 3-mercaptopropyltrimethoxysilane, 3-mercaptopropyltriethoxysilane, 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane. Other organosilicon compounds have been described in WO 99/09036, EP 1 108 231, DE 101 37 809, DE 101 63 945, DE 102 23 658.

In one preferred embodiment of the invention, bis(3-triethoxysilylpropyl) tetrasulfane may be used as silane.

The silica of the invention may be incorporated as reinforcing filler in elastomer mixtures, tires, or vulcanizable rubber mixtures, in amounts of from 5 to 200 parts, based on 100 parts of rubber, in the form of powder, beads, or pellets, either with silane modification or else without silane modification.
For the purposes of the present invention, rubber mixtures and elastomer mixtures are regarded as equivalent.

The silanol groups on the silica surface function in rubber mixtures as possible chemical reaction partners for a coupling reagent. By way of example, this is a bifunctional silane, such as bis(3-triethoxysilylpropyl) tetrasulfane, which permits the linkage of the silica to the rubber matrix. The maximum number of silanol groups therefore achieves high probability of coupling between silica and the coupling reagent, and thus high probability of linkage of the silica to the rubber matrix, the final result of this being higher reinforcing potential. The Sears value V_2 is a

dimension allowing description of the number of silanol
groups in the silica, while the BET surface area of a
silica describes its specific surface area, which has a
major effect on the processing behavior of a compounded
5   material, and on its other properties after
vulcanization. However, the data relating to the
absolute number of silanol groups are not themselves
sufficient for adequate characterization of a
precipitated silica, because precipitated silicas with
10 a high surface area generally have a higher absolute
number of silanol groups than precipitated silicas with
a low surface area. The important factor is therefore
the quotient calculated by dividing the Sears value V_2
by the BET. In this way it is possible to represent the
15 reinforcement potential generated via the silanol
groups per unit of specific surface area introduced.

The fillers in the elastomer mixtures or rubber
mixtures may comprise not only mixtures comprising
20 exclusively the silicas of the invention, with or
without the abovementioned organosilanes but also one
or more other fillers with relatively high or
relatively low reinforcing capability.

25 The other fillers used may comprise the following
materials:
- Carbon blacks: the carbon blacks to be used here are
  prepared by the flame black process, furnace black
  process, or gas black process, and have BET surface
30 areas of from 20 to 200 m^2/g, e.g. SAF, ISAF, HSAF,
  HAF, FEF, or GPF blacks. Where appropriate, the
  carbon blacks may also contain heteroatoms, e.g.
  silicon.
- Fine-particle fumed silicas, e.g. prepared by flame
35 hydrolysis of silicon halides. Where appropriate, the
  silicas may also be mixed oxides with other metal
  oxides, such as Al oxides, Mg oxides, Ca oxides, Ba
  oxides, Zn oxides, or titanium oxides.

- Other commercially available silicas.
- Synthetic silicates, such as aluminum silicate, or alkaline earth metal silicates, such as magnesium silicate or calcium silicate, with BET surface areas of from 20 to 400 m^2/g and with primary particle diameters of from 10 to 400 nm.
- Synthetic or natural aluminum oxides and synthetic or natural aluminum hydroxides.
- Natural silicates, such as kaolin, and other naturally occurring silicon dioxide compounds.
- Glass fiber and glass fiber products (mats, strands), or glass microbeads.
- Starch and modified grades of starch.
- Naturally occurring fillers, e.g. clays and siliceous chalk.

Here, as with the amounts used of the organosilanes, the mixing ratio depends on the property profile to be achieved in the finished rubber mixture. A conceivable ratio, also implemented here, between the silicas of the invention and the other abovementioned fillers (including a mixture) is 5-95%.

In one particularly preferred embodiment, from 10 to 150 parts by weight of silicas, composed entirely or to some extent of the silica of the invention, may be used to prepare the mixtures, where appropriate together with from 0 to 100 parts by weight of carbon black, use may also be made of from 1 to 10 parts by weight of an organosilicon compound, based in each case on 100 parts by weight of rubber.

Another important constituent of the rubber mixture, besides the silicas of the invention, the organosilanes, and other fillers, is the elastomers. Mention may be made here of elastomers, natural or synthetic, oil-extended or non-oil-extended, in the form of single polymer or blend with other rubbers,

examples being natural rubbers, polybutadiene (BR),
polyisoprene (IR), styrene/butadiene copolymers having
styrene contents of from 1 to 60% by weight, preferably
from 2 to 50% by weight (SBR), in particular prepared
5   by means of the solution polymerization process, butyl
rubbers, isobutylene-isoprene copolymers (IIR),
butadiene-acrylonitrile copolymers having acrylonitrile
contents of from 5 to 60% by weight, preferably from 10
to 50% by weight (NBR), partially or fully hydrogenated
10   NBR rubber (HNBR), ethylene-propylene-diene copolymers
(EPDM), or else a mixture of these rubbers.

The following additional rubbers may also be used for
rubber mixtures with the rubbers mentioned:
15   carboxy rubbers, epoxy rubbers, trans-polypentenamers,
halogenated butyl rubbers, 2-chlorobutadiene rubbers,
ethylene-vinyl acetate copolymers, ethylene-propylene
copolymers, and, where appropriate, also chemically
derivatized natural rubber, and also modified natural
20   rubbers.
By way of example, W. Hofmann, "Kautschuktechnologie"
[Rubber technology], Genter Verlag, Stuttgart, 1980,
describes preferred synthetic rubbers.
Anionically polymerized SSBR rubbers (solution SBRs)
25   with a glass transition temperature above -50°C are of
particular interest for producing the tires of the
invention, as are mixtures of these with diene rubbers.

The silicas of the invention, with or without silane,
30   may be used in any of the applications of rubbers, for
example moldings, tires, tire treads, conveyor belts,
gaskets, drive belts, hoses, shoe soles, cable
sheathing, roller coverings, damping elements, etc.

35   The incorporation of this silica and the preparation of
the mixtures comprising this silica, take place in an
internal mixer or on a roll mill, preferably at
80-200°C, in the manner conventional in the rubber

industry. The form in which the silicas are used may be either powder, beads, or pellets. Again, there is no difference between the silicas of the invention and the known pale-color fillers.

5

The rubber vulcanizates of the invention may comprise the usual amounts of other rubber auxiliaries, such as reaction accelerators, antioxidants, heat stabilizers, light stabilizers, ozone stabilizers, processing aids,

10 plasticizers, tackifiers, blowing agents, dyes, pigments, waxes, extenders, organic acids, retarders, metal oxides, and also activators, such as triethanolamine, polyethylene glycol, and hexanetriol. These compounds are known in the rubber industry.

15

The amounts which may be used of the rubber auxiliaries are those which are known, and depend, inter alia, on the intended use. Examples of usual amounts are from 0.1 to 50% by weight, based on the rubber used. Sulfur

20 or sulfur-donor substances may be used as crosslinkers. The rubber mixtures of the invention may moreover comprise vulcanization accelerators. Examples of suitable primary accelerators are mercaptobenzothiazoles, sulfenamides, thiurames, and

25 dithiocarbamates in amounts of from 0.5 to 3% by weight. Examples of coaccelerators are guanidines, thioureas, and thiocarbonates in amounts of from 0.5 to 5% by weight. The amounts of sulfur which may usually be used are from 0.1 to 10% by weight, preferably from

30 1 to 3% by weight, based on the rubber used.

The silicas of the invention may be used in rubbers which are crosslinkable using accelerators and/or sulfur, or else peroxidically crosslinkable.

35

The rubber mixtures of the invention may be vulcanized at temperatures of from 100 to 200°C, preferably from 130 to 180°C, where appropriate under a pressure of

from 10 to 200 bar. Known mixing assemblies, such as roll mills, internal mixers, and mixing extruders, may be used for blending of the rubbers with the filler, where appropriate with rubber auxiliaries, and with the

5   organosilicon compound.

The rubber mixtures of the invention are suitable for producing moldings, for example for producing pneumatic tires, tire treads for tires for summer, winter, or

10   year-round use, car tires, tires for utility vehicles, motorcycle tires, tire carcass components, cable sheathing, hoses, drive belts, conveyor belts, roller coverings, shoe soles, gasket ring seals, and damping elements.

15

An advantage of the silicas of the invention is that they are highly dispersible and that their low microporosity gives them higher rubber activity with respect to the rubber vulcanizates, and that they

20   therefore provide greater reinforcement to the rubber vulcanizates.

When comparison is made with an identical rubber mixture using a prior-art silica, the silicas of the

25   invention also exhibit advantages in vulcanization time.

The rubber mixtures of the invention are particularly suitable for producing tire treads for car tires and

30   for motor cycle tires, and also for producing utility vehicle tires with reduced rolling resistance together with good abrasion resistance and good suitability for winter conditions.

35   The rubber mixtures of the invention are also suitable, without addition of organosilicon compounds, blended with a typical tire tread carbon black, for improving the cut & chip performance of tires on construction

machinery, on agricultural machinery, or tires used in
mining. (For definitions and further details see "New
insights into the tear mechanism" and references cited
therein, presented by Dr. W. Niedermeier at Tire Tech
5   2003 in Hamburg.)

The reaction conditions and the physico-chemical data
for the precipitated silicas of the invention are
determined using the following methods:
10

Determination of moisture level of silicas

Based on ISO 787-2, this method is used to determine
the volatile content (hereinafter termed moisture level
15 for simplicity) of silica after drying for 2 hours at
105°C. This loss on drying is generally composed mainly
of moisture.

Method
20

10 g of the silica in powder, bead, or pellet form are
weighed out precisely to 0.1 mg into a dry glass
weighing vessel with ground-glass lid (diameter 8 cm,
height 3 cm) (specimen weight E). With the lid open,
25 the specimen is dried for 2 h at 105 ± 2°C in a drying
cabinet. The glass weighing vessel is then sealed, and
cooled to room temperature in a desiccator cabinet,
using silica gel as drying agent. The specimen is
weighed to give the final weight A.
30 The moisture level in % is determined as ((E in g - A
in g)*100%)/(E in g).

Determination of modified Sears value of silicas

35 The modified Sears value (hereinafter termed Sears
value V_2) can be determined by titrating silica with
potassium hydroxide solution in the range from pH 6 to
pH 9, and is a measure of the number of free hydroxy

groups.

The following chemical reactions underlie the determination method, "Si"-OH being intended to symbolize a silanol group of the silica:

5   "Si"-OH + NaCl → "Si"-ONa + HCl

HCl + KOH   → KCl + H_2O.
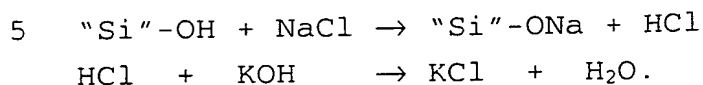
Method

10   10.00 g of a silica in powder, bead or pellet form, having a moisture level of 5 ± 1%, are comminuted for 60 seconds, using an M 20 IKA universal mill (550 W; 20 000 rpm). Where appropriate, the moisture content of the starting substance has to be adjusted by drying at

15   105°C in the drying cabinet or uniform moistening, with repeated comminution. 2.50 g of the silica thus treated are weighed out at room temperature into a 250 ml titration vessel and mixed with 60.0 ml of analytical grade methanol. After complete wetting of the specimen,

20   40.0 ml of deionized water are added, and the mixture is dispersed, using a T 25 UltraTurrax mixer (KV-18G mixing shaft, 18 mm diameter) for 30 seconds at a rotation rate of 18 000 rpm. The particles of specimen adhering to the edge of the vessel and to the stirrer

25   are flushed into the suspension, using 100 ml of deionized water, and a water bath with thermostat is used to control the temperature of the mixture to 25°C. The pH tester (Knick 766 Calimatic pH meter with temperature sensor) and pH electrode (Schott N7680

30   combination electrode) are calibrated using buffer solutions (pH 7.00 and 9.00) at room temperature. Using the pH meter, the initial pH of the suspension is first measured at 25°C, and then, depending on the result, potassium hydroxide solution (0.1 mol/l) or

35   hydrochloric acid solution (0.1 mol/l) is used to adjust the pH to 6.00. The consumption of KOH solution or HCl solution in ml required to reach pH 6.00 corresponds to V_1'.

20.0 ml of sodium chloride solution (250.00 g of analytical grade NaCl made up to 1 l using deionized water) are then metered in. The titration is then continued as far as pH 9.00, using 0.1 mol/l KOH. The

5   consumption of KOH solution in ml required to reach pH 9.00 corresponds to V_2'.
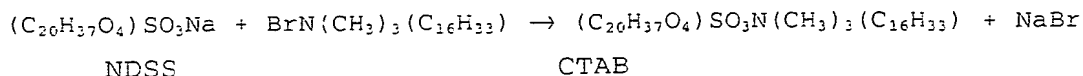
The volumes V_1' and V_2' are first then normalized for a theoretical specimen weight of 1 g, and are then multiplied by 5, thus giving V_1 and the Sears value V_2

10   in the units ml/(5 g).

Determination of BET surface area

The specific nitrogen surface area (hereinafter termed

15   BET surface area) of the silica in powder, bead, or pellet form is determined to ISO 5794-1/Annex D, using an AREA-meter (Ströhlein, JUWE).

CTAB surface area determination

20

The method is based on the adsorption of CTAB (N-hexadecyl-N,N,N-trimethylammonium bromide) on the "external" surface of the silica, also termed the "rubber-active surface", and is based on ASTM3765 or

25   NFT 45-007 (Section 5.12.1.3). CTAB is adsorbed in aqueous solution, with stirring and treatment with ultrasound. Excess, unadsorbed CTAB is determined by back-titration with NDSS (solution of the sodium salt of dioctyl sulfosuccinate, "Aerosol OT" solution),

30   using a titroprocessor, the end point being given by maximum clouding of the solution, and determined using a phototrode. The temperature during all of the operations carried out is 23-25°C, in order to prevent CTAB from crystallizing out. The following equation

35   underlies the back-titration reaction:

$$(C_{20}H_{37}O_4)SO_3Na + BrN(CH_3)_3(C_{16}H_{33}) \rightarrow (C_{20}H_{37}O_4)SO_3N(CH_3)_3(C_{16}H_{33}) + NaBr$$

NDSS   CTAB

Equipment

METTLER Toledo DL 55 titroprocessor and METTLER Toledo
DL 70 titroprocessor, in each case equipped with:
DG 111 pH electrode produced by Mettler, and DP 550
phototrode produced by Mettler
100 ml polypropylene titration beaker
150 ml glass titration vessel with lid
Pressure-filtration equipment, capacity 100 ml
Membrane filter composed of cellulose nitrate, pore
size 0.1 μm, diameter 47 mm, e.g. Whatman (order no.
7181-004)

Reagents

The solutions of CTAB (0.015 mol/l in deionized water)
and NDSS (0.00423 mol/l in deionized water) are
purchased in ready-to-use form (Kraft, Duisburg: order
no. 6056.4700 CTAB solution, 0.015 mol/l; order no.
6057.4700 NDSS solution, 0.00423 mol/l), stored at
25°C, and used within one month.

Method

Blind titration

The consumption of NDSS solution for the titration of
5 ml of CTAB solution is to be tested once daily prior
to each series of tests. For this, the phototrode is
adjusted to 1000 $\pm$ 20 mV (corresponding to 100%
transparency) prior to starting the titration.
Exactly 5.00 ml of CTAB solution are pipetted into a
titration beaker, and 50.0 ml of deionized water are
added. The titration with NDSS solution uses the test
method familiar to the person skilled in the art, with
stirring, using the DL 55 titroprocessor until max.
clouding of the solution has been reached. The

consumption V_I of NDSS solution is determined in ml. Three determinations are to be carried out for each titration.

5 **Adsorption**

10.0 g of the silica in powder, bead or pellet form, with a moisture content of 5 $\pm$ 2% (the moisture content being adjusted, where appropriate, by drying at 105°C
10 in the drying cabinet or uniform moistening), are comminuted for 30 seconds, using a mill (Krups KM 75, item no. 2030-70). Exactly 500.0 mg of the comminuted specimen are transferred into a 150 ml titration vessel with magnetic stirrer bar, and exactly 100.0 ml of CTAB
15 solution are metered in. The titration vessel is sealed with a lid, and the mixture is stirred for 15 minutes, using a magnetic stirrer. Hydrophobic silicas are stirred, using a T 25 UltraTurrax mixer (KV-18G mixer shaft, 18 mm diameter), at 18 000 rpm for a maximum of
20 1 min to give complete wetting. The titration vessel is screw-fastened to the DL 70 titroprocessor, and the pH of the suspension is adjusted to a value of 9 $\pm$ 0.05, using KOH (0.1 mol/l). The suspension is exposed for 4 minutes to ultrasound, in the titration vessel, in an
25 ultrasound bath (Sonorex RK 106 S from Bandelin, 35 KHz) at 25°C. This is followed immediately by filtration under pressure through a membrane filter, the nitrogen pressure being 1.2 bar. The first 5 ml of filtrate are discarded.
30

Titration

5.00 ml of the remaining filtrate are pipetted into a 100 ml titration beaker and made up to 50.00 ml, using
35 deionized water. The titration beaker is screw-fastened to the DL 55 titroprocessor, and the mixture is titrated with NDSS solution, with stirring, until maximum clouding has been reached. The consumption V_{II}

of NDSS solution in ml is determined. Each clouding point is to be determined three times.

Calculation

5

The measured values

V_I =   consumption of NDSS solution in ml when the blind specimen is titrated

V_{II} =   consumption of NDSS solution in ml when the filtrate is used

give:

V_I/V_{II} = amount of CTAB in the blind specimen/remaining amount of CTAB present in the filtrate specimen.

The amount N of adsorbed CTAB in g is therefore:

$N = ((V_I-V_{II}) * 5.5 \text{ g} * 5 \text{ ml})/V_I*1000 \text{ ml})$.

Because only 5 ml were titrated from 100 ml of

10 filtrate, and 0.5 kg of silica of a defined moisture level was used, and the area required by 1 g of CTAB is $578435 * 10^{-3} \text{ m}^2$ and:

CTAB surface area (not corrected for water) in m^2/g = $(N*20*578.435 \text{ m}^2/\text{g})/(0.5 \text{ g})$, and

15 CTAB surface area (not corrected for water) in m^2/g = $((V_I-V_{II})* 636.2785 \text{ m}^2/\text{g})/V_I$.

The CTAB surface area is based on the anhydrous silica, and the following correction is therefore made:

CTAB surface area in m^2/g = (CTAB surface area (not

20 corrected for water) in m^2/g * 100%)/(100% - moisture level in %).

Determination of DBP absorption

25 DBP absorption (DBP number) is determined as follows by a method based on the standard DIN 53601, and is a measure of the absorbency of the precipitated silica:

Method

12.50 g of silica in powder or bead form with 0-10%
5   moisture content (the moisture content being adjusted,
where appropriate, by drying at 105°C in the drying
cabinet) are placed in the kneader chamber (item no.
279061) of the Brabender "E" Absorptometer (with no
damping of the output filter of the torque sensor). In
10 the case of pellets, the sieve fraction from 3.15 to
1 mm (Retsch stainless-steel sieve) is used (by using
slight pressure from a plastics spatula to press the
pellets through the 3.15 mm-pore-width sieve). While
the material is constantly mixed (rotation rate of
15 kneader paddles: 125 rpm), dibutyl phthalate is added
dropwise at a rate of 4 ml/min at room temperature into
the mixture by way of the "Brabender T 90/50 Dosimat".
Incorporation by mixing is achieved with only low power
consumption, and is followed by means of the digital
20 display. Toward the end of the determination, the
mixture becomes pasty, and this is indicated by a steep
rise in the power consumption. When the display shows
600 digits (0.6 Nm torque), both the kneader and the
DBP feed are switched off via an electrical contactor.
25 The synchronous motor for the DBP supply has coupling
to a digital meter, thus permitting read-off of DBP
consumption in ml.

Evaluation
30

DBP absorption is stated in g/(100 g), and is
calculated from the measured DBP consumption by using
the following formula. The density of DBP at 20°C is
typically 1.047 g/ml.
35 DBP absorption in g/(100 g) = ((DBP consumption in ml)
* (DBP density in g/ml) * 100)/(12.5 g).

Defined DBP absorption relates to the anhydrous, dried

silica. If moist precipitated silicas are used, the value is to be corrected by means of the following correction table. The correction value, corresponding to the water content, is added to the DBP value determined experimentally; by way of example, an addition of 33 g/(100 g) for DBP absorption would be implied if the water content were 5.8%.

Correction table for dibutyl phthalate absorption – anhydrous –

% water	.% water				
	.0	.2	.4	.6	.8
0	0	2	4	5	7
1	9	10	12	13	15
2	16	18	19	20	22
3	23	24	26	27	28
4	28	29	29	30	31
5	31	32	32	33	33
6	34	34	35	35	36
7	36	37	38	38	39
8	39	40	40	41	41
9	42	43	43	44	44
10	45	45	46	46	47

pH determination

The method, based on DIN EN ISO 787-9, serves for determination of the pH of an aqueous suspension of silicas at 20°C. To this end, an aqueous suspension is prepared from the specimen to be studied. After brief shaking of the suspension, its pH is determined by means of a previously calibrated pH meter.

Method

Prior to making the pH measurement, daily calibration of the pH tester (Knick 766 Calimatic pH meter with

temperature sensor) and of the pH electrode (Schott
N7680 combination electrode, is required, using the
buffer solutions, at 20°C. The calibration function is
to be selected in such a way that the two buffer
5   solutions used include the expected pH of the specimen
(buffer solutions having pH 4.00 and 7.00, pH 7.00 and
9.00, and, where appropriate, pH 7.00 and 12.00). If
pellets are used, 20.0 g of silica are first comminuted
for 20 s by means of a mill (Krups KM 75, item No.
10 2030-70).
5.00 g of silica in powder or bead form, with 5 ± 1%
moisture content (where appropriate, the moisture
content being adjusted by drying at 105°C in the drying
cabinet or by uniform wetting prior to any comminution)
15 are precisely weighed out to 0.01 g on a precision
balance into a previously tared wide-necked glass
flask. 95.0 ml of deionized water are added to the
specimen. An automatic shaker (Gerhardt, LS10, 55 W,
level 7) is then used to shake the suspension in the
20 sealed vessel for a period of 5 minutes at room
temperature. The pH is measured directly after shaking.
To this end, the electrode is rinsed first with
deionized water and then with a portion of the
suspension, and then dipped into the suspension. A
25 magnetic stirrer bar is then added to the suspension,
and the pH measurement is made at a constant stirring
rate with formation of slight vortex in the suspension.
When the pH meter displays a constant value, the pH is
read off from the display.

30

The method when hydrophobic silica is used is similar,
but in that case 5.00 g of the specimen, after
comminution where appropriate and with 5 ± 1% moisture
content, are weighed out precisely to 0.01 g on the
35 precision balance into a previously tared wide-necked
glass flask. 50.0 ml of analytical grade methanol and
50.0 ml of deionized water are added, and an automatic
shaker (Gerhardt, LS10, 55 W, level 7) is then used to

shake the suspension in the sealed vessel for a period
of 5 minutes at room temperature. The pH is likewise
measured with stirring, but after precisely 5 min.

Determination of solids content of filter cake

This method is used to determine the solids content of
filter cake via removal of the volatile content at
105°C.

Method

100.00 g of the filter cake are weighed out into a dry,
tared porcelain dish (diameter 20 cm) (specimen
weight E). Where appropriate, the filter cake is
comminuted, using a spatula, in order to obtain
separate fragments of not more than 1 cm^3. The specimen
is dried to constant weight at 105 ± 2°C in a drying
cabinet. The specimen is then cooled to room
temperature in a desiccator cabinet, using silica gel
as drying agent. The material is weighed to determine
the final weight A.
The solids content in % is determined as 100% - (((E in
g - A in g)*100%)/(E in g)).

Determination of electrical conductivity

The electrical conductivity (C) of silicas is
determined in aqueous suspension.

Method

If pellets are used, 20.0 g of silica are first
comminuted by means of a mill (Krups, KM 75, item No.
2030-70) for 20 s. 4.00 g of silica in powder or bead
form, with 5 ± 1% moisture content (the moisture
content being adjusted, where appropriate, by drying at
105°C in the drying cabinet or uniform wetting prior to

any comminution) are suspended in 50.0 ml of deionized water, and heated for 1 min to 100°C. The specimen cooled to 20°C is made to precisely 100 ml and homogenized by rotary shaking.

5   The measurement cell of the LF 530 (WTW) conductivity tester is flushed with a small amount of specimen before the LTA01 measurement cell is dipped into the suspension. The value displayed corresponds to the conductivity at 20°C, because the TFK 530 external

10   temperature sensor automatically compensates for the temperature. Both this temperature coefficient and the cell constant k are to be checked prior to each series of tests.

The calibration solution used comprises 0.01 mol/l

15   potassium chloride solution (C at 20°C = 1278 μS/cm).

Determination of solids content of precipitation suspension

20   The solids content of the precipitation suspension is determined gravimetrically after filtration of the specimen.

Method

25

100.0 ml of the homogenized precipitation suspension ($V_{suspension}$) are measured out at room temperature with the aid of a measuring cylinder. The specimen is filtered off with suction by way of a round filter

30   (Schleicher & Schuell 572) in a porcelain suction filter funnel, but not sucked dry, so as to avoid cracking of the filter cake. The filter cake is then washed with 100.0 ml of deionized water. The suction-filtration of the leached filter cake is then

35   completed, and the filter cake is transferred into a tared porcelain dish and dried to constant weight at 105 ± 2°C in a drying cabinet. The weight of the dried silica ($m_{specimen}$) is determined.

The solids content is determined as:

solids content in g/l = $(m_{specimen}$ g$)/(V_{suspension}$ in l$)$.

Determination of alkali value

5

The alkali value (AV) determined is the consumption in ml of hydrochloric acid (using a specimen volume of 50 ml, 50 ml of dist. water, and a hydrochloric acid concentration of 0.5 mol/l) during direct

10 potentiometric titration of alkaline solutions or alkaline suspensions as far as pH 8.30. The result reveals the free alkali content of the solution or suspension.

15 Method

The pH device (Knick, Calimatic 766 pH meter with temperature sensor) and the pH electrode (Schott N7680 combination electrode) are calibrated at room

20 temperature with the aid of two buffer solutions (pH = 7.00 and pH = 10.00). The combination electrode is dipped into the test solution or test suspension, the temperature of which has been controlled to 40°C, and which is composed of 50.0 ml of specimen and 50.0 ml of

25 deionized water. Hydrochloric acid solution whose concentration is 0.5 mol/l is then added dropwise until a constant pH of 8.30 is obtained. Because the equilibrium between the silica and the free alkali content is established only slowly, a waiting time of

30 15 min is required before final read-off of the acid consumption. For the amounts and concentrations selected, the read-off of hydrochloric acid consumption in ml directly corresponds to the alkali value, which is a dimensionless quantity.

35

The following examples are intended to provide further illustration of the invention but not to limit its scope.

Example 1

Silica I

1550 l of water and 141.4 kg of water glass (density 1.348 kg/l, 27.0% SiO_2, 8.05% Na_2O) form an initial charge in a reactor made from stainless steel with a propeller-stirrer system and jacket heating. 5.505 kg/min of the abovementioned water glass and about 0.65 kg/min of sulfuric acid (density 1.83 kg/l, 96% H_2SO_4) are then metered in with vigorous stirring at 92°C over a period of 80 minutes. This metering of sulfuric acid is regulated in such a way that the alkali value prevailing in the reaction mixture is 20. The water glass addition is then stopped, and the addition of sulfuric acid is continued until a pH of 9.0 (measured at room temperature) has been achieved. The sulfuric acid addition is stopped, and stirring of the resultant suspension is continued for 60 minutes at 90°C. Addition of sulfuric acid is then restarted, and a final pH of 3.5 (measured at room temperature) is established.
The resultant suspension is filtered, using a membrane filter press, and the product is washed with water. The filter cake, with 23% solids content, is liquidized, using aqueous sulfuric acid and a shearing assembly. The silica feed with 19% solids content and with a pH of 3.7 is then spray-dried with addition of ammonia. The resultant powder Ia has a BET surface area of 114 m^2/g and a CTAB surface area of 123 m^2/g. The spray-tower-dried microbead product Ib obtained as an alternative has a BET surface area of 126 m^2/g and a CTAB surface area of 123 m^2/g.

Silica II

1550 l of water and 141.4 kg of water glass (density

1.348 kg/l, 27.0% SiO_2, 8.05% Na_2O) form an initial charge in a reactor made from stainless steel with a propeller-stirrer system and jacket heating. 5.505 kg/min of the abovementioned water glass and about 0.65 kg/min of sulfuric acid (density 1.83 kg/l, 96% H_2SO_4) are then metered in with vigorous stirring at 92°C over a period of 80 minutes. This metering of sulfuric acid is regulated in such a way that the alkali value prevailing in the reaction mixture is 20. The water glass addition is then stopped, and the addition of sulfuric acid is continued until a pH of 7.0 (measured at room temperature) has been achieved. The sulfuric acid addition is stopped, and stirring of the resultant suspension is continued for 60 minutes at 90°C. Addition of sulfuric acid is then restarted, and a final pH of 3.5 (measured at room temperature) is established.

The resultant suspension is filtered, using a membrane filter press, and the product is washed with water. The filter cake, with 22% solids content, is liquidized, using aqueous sulfuric acid and a shearing assembly. The silica feed with 19% solids content and with a pH of 3.6 is then spray-tower-dried with addition of ammonia.

The resultant microbead product has a BET surface area of 116 m^2/g and a CTAB surface area of 117 m^2/g.

Silica III

1550 l of water and 141.4 kg of water glass (density 1.348 kg/l, 27.0% SiO_2, 8.05% Na_2O) form an initial charge in a reactor made from stainless steel with a propeller-stirrer system and jacket heating. 5.505 kg/min of the abovementioned water glass and about 0.65 kg/min of sulfuric acid (density 1.83 kg/l, 96% H_2SO_4) are then metered in with vigorous stirring at 92°C over a period of 100 minutes. This metering of sulfuric acid is regulated in such a way that the

alkali value prevailing in the reaction mixture is 20. The water glass addition is then stopped, and the addition of sulfuric acid is continued until a pH of 9.0 (measured at room temperature) has been achieved.

5   The sulfuric acid addition is stopped, and stirring of the resultant suspension is continued for 60 minutes at 90°C. Addition of sulfuric acid is then restarted, and a final pH of 3.5 (measured at room temperature) is established.

10 The resultant suspension is filtered, using a membrane filter press, and the product is washed with water. The filter cake, with 23% solids content, is liquidized, using aqueous sulfuric acid and a shearing assembly. The silica feed with 19% solids content and with a pH

15 of 3.8 is then spray-dried with addition of ammonia. The resultant product has a BET surface area of 102 m^2/g and a CTAB surface area of 104 m^2/g.

The physical data for the above silicas are given in

20 the table below:

		Silica Ia	Silica Ib	Silica II	Silica III	REF Ultrasil 7000 GR
Finishing		pH 9	pH 9	pH 7	pH 9	---
Moisture level	[%]	4.5	5.1	5.1	5.0	5.4
pH	[-]	5.6	5.5	5.5	5.6	6.2
Conductivity	[μS/cm]	610	550	600	590	620
BET	[m^2/g]	114	126	116	102	174
CTAB	[m^2/g]	123	123	117	104	163
BET/CTAB	[-]	0.93	1.02	0.99	0.98	1.07
DBP	[g/(100 g)]	278	258	274	256	228
Sears value V_2	[ml/(5 g)]	22	21	22	22	16
Sears value V_2/BET	[ml/(5 m^2)]	0.193	0.167	0.190	0.216	0.092

Example 2

25 The precipitated silicas Ib and II of the invention from Example 1 were studied in an SSBR/BR rubber mixture. The readily dispersible silica Ultrasil 7000

GR (Reference) from Degussa AG was selected as prior art.

The mixing specification used for the rubber mixtures is given in Table 1 below. The unit phr here means parts by weight, based on 100 parts of the untreated rubber used.

Table 1

1st stage	
Buna VSL 5025-1	96
Buna CB 24	30
Silica	80
X50-S	12.8
ZnO	2
Stearic acid	2
Naftolen ZD	10
Vulkanox 4020	1.5
Protector G 3108	1
2nd stage	
Stage 1 batch	
3rd stage	
Stage 2 batch	
Vulkacit D/C	2.0
Vulkacit CZ/EG	1.5
Perazit TBZTD	0.2
Sulfur	1.2

The polymer VSL 5025-1 is a solution-polymerized SBR copolymer from Bayer AG with a styrene content of 25% by weight and a butadiene content of 75% by weight. The copolymer comprises 37.5 phr of oil and has a Mooney viscosity (ML 1+4/100°C) of 50 ± 4. The polymer Buna CB 24 is a cis-1,4-polybutadiene (neodymium grade) from Bayer AG with cis-1,4 content of at least 97% and a Mooney viscosity of 44 ± 5.

X50-S is a 50/50 blend of Si 69 [bis(3-triethoxysilyl-propyl) tetrasulfide] and carbon black obtainable from Degussa AG.

The aromatic oil used comprises Naftolen ZD from
Chemetall. Vulkanox 4020 is 6PPD from Bayer AG. and
Protektor G 3108 is an ozone-protection wax from HB-
Fuller GmbH. Vulkacit D/C (DPG) and Vulkacit CZ/EG
5   (CBS) are commercially available products from Bayer
AG. Perkazit TBZTD is obtainable from Akzo Chemie GmbH.
The rubber mixtures are prepared in an internal mixer
using the mixing instructions in Table 2. Table 3 gives
the methods used for rubber testing. The mixtures are
10 vulcanized at 165°C for 20 minutes. Table 4 shows the
results of testing on the vulcanized rubber.

Table 2

Stage 1	
Settings	
Mixing assembly	Werner & Pfleiderer 1.5N
Rotation rate	70 rpm
Friction	1:1.11
Ram pressure	5.5 bar
Capacity	1.6 1
Fill level	0.73
Chamber temp.	70°C
Mixing procedure	
0-0.5 min	Buna VSL 5025-1 + Buna CB 24
0.5-1.5 min	1/3 filler, X50-S
1.5-2.5 min	1/3 filler
2.5-3.5 min	1/3 filler, remaining stage 1 constituents
3.5-4.5 min	mixing
4.5-6.0 min	mixing and discharge
Storage	24 h at room temperature

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Stage 2	
Settings	
Mixing assembly	as in stage 1 except:
Rotation rate	80 rpm
Chamber temp.	80°C
Fill level	0.71
Mixing procedure	
0-5 min	stage 1 batch, maintain batch temperature 140-150°C by varying rotation rate
5 min	discharge
Storage	4 h at room temperature

Stage 3	
Settings	
Mixing assembly	as in stage 1 except:
Rotation rate	40 rpm
Chamber temp.	50°C
Fill level	0.69
Mixing procedure	
0-2 min	stage 2 batch, stage 3 constituents
2 min	discharge and form milled sheet on laboratory roll mill, (diameter 200 mm, length 450 mm, roll temperature 50°C) homogenization: cut the material 3 times toward the left, 3 times toward the right fold the material over 5 times with narrow roll gap (1 mm) and 5 times with wide roll gap (3.5 mm) and peel milled sheet away

Table 3

Physical testing	Standard/conditions
Vulcameter testing, 165°C	DIN 53529/3, ISO 6502
Torque difference Dmax-Dmin [dNm]	
t10% and t90% [min]	
Ring tensile test, 23°C	DIN 53504, ISO 37
Stress values 100% and 300% [Mpa]	
Reinforcement factor: stress value 300%/100% [-]	
Shore A hardness, 23°C [-]	DIN 53 505
Ball rebound [%], 0°C and 60°C	DIN EN ISO 8307
	steel ball, 19 mm, 28 g
Dispersion coefficient [%]	see text
Viscoelastic properties, 0 and 60°C, 16 Hz, initial force 50 N and amplitude force 25 N Test value recorded after 2 min. of test time, i.e. 2 min. of conditioning	DIN 53 513, ISO 2856
Complex modulus E* [Mpa]	
Loss factor tan δ [-]	

The dispersion coefficient was determined using the surface topography inc. Medalia correction (A. Wehmeier, "Filler Dispersion Analysis by Topography Measurements" Technical Report TR 820, Degussa AG, Advanced Fillers and Pigments Division). The dispersion coefficient thus determined correlates at reliability level > 0.95 with the optically determined dispersion coefficient, for example as determined by the Deutschen Institut für Kautschuktechnologie e.V. [Germany Institute for Rubber Technology], Hanover, Germany (H. Geisler, Bestimmung der Mischgüte, presented at DIK Workshop, 27-28 November 1997, Hanover, Germany).

Table 4

Data for untreated mixture	REF	Silica Ib	Silica II
Dmax-Dmin	16.4	16.5	16.1
t10%	1.4	1.8	1.8
t90%	6.2	5.5	5.6
Vulcanizate data			
100% stress	1.7	2.1	2.1
300% stress	9.2	12.3	12.4
300%/100% stress	5.4	5.9	5.9
Shore A hardness	62	64	63
Ball rebound 0°C	15.8	15.1	14.8
Ball rebound 60°C	62.5	64.2	64.4
E* (0°C)	19.2	19.0	18.2
E* (60°C)	7.7	7.9	7.7
tan δ (0°C)	0.475	0.460	0.454
tan δ (60°C)	0.124	0.108	0.106
Dispersion coefficient	94	96	97

As can be seen from the data in Table 4, the Silica Ib and Silica II mixtures with the silicas of the invention have a lower vulcanization time t90% than the reference mixture REF, due to lower microporosity and therefore less surface-adsorption of accelerator. The advantageous higher activity of these silicas is reflected in the higher 100% and 300% stress values and the increased reinforcement factor. The dynamic properties of the mixtures with the silicas of the invention have likewise been improved. Ball rebound 0°C is found to be lower, implying improved wet skid resistance, and ball rebound 60°C is found to be higher, indicating better rolling resistance of a tire tread. The dynamic stiffnesses at 0 and 60°C are at the same level as those of the reference mixture, while the hysteresis loss tan δ (60°C) has an advantageously been lowered, indicating lower rolling resistance. In addition, the quality of dispersion of the silicas of the invention is extraordinarily high and, inter alia,

better than that of the silica Ultrasil 7000 GR of the prior art, which itself has good dispersibility, thus achieving advantages in road abrasion.